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(21) International Application Number: PCT/US95/14429 (22) International Filing Date: 8 November 1995 (08.11.95) (30) Priority Data: PM 9304 9 November 1994 (09.11.94) AU (71) Applicants (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION [AU/AU]; 407 Royal Parade, Parkville, VIC 3052 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): MOAD, Graeme [AU/AU]; 137 Monbulk Road, Kallista, VIC 3791 (AU). MOAD, Catherine, Louise [US/AU]; 137 Monbulk Road, Kallista, VIC 3791 (AU). KRSTINA, Julia [AU/AU]; 16B Elsie Grove, Chelsea, VIC 3196 (AU). RIZZARDO, Ezio [AU/AU]; 26 Alex Avenue, Wheelers Hill, VIC 3150 (AU). THANG, San, Hoa [AU/AU]; 180 Clarinda Road, Clayton South, VIC 3169 (AU). FRYD, Michael [US/US]; 50 East Maple Avenue, Moorestown, NJ 08057-1910 (US).		(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AL, AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERIZATION IN AQUEOUS MEDIA (57) Abstract A method for the solution or emulsion polymerization of ethylenically unsaturated monomers, styrene, and other free radical polymerizable monomers in aqueous media in which a cobalt chain transfer agent is used which has both hydrolytic stability and solubility in water and in the organic phase with preferential solubility in the organic phase.		

TITLE
POLYMERIZATION IN AQUEOUS MEDIA

FIELD OF INVENTION

5 This invention relates to free-radical polymerization in emulsion or in aqueous solution to produce polymers with defined molecular weight and end group structures and to certain cobalt complexes employed in the polymerization process.

BACKGROUND ART

10 US 5 324 879 discloses the use of cobalt(III) complexes to control molecular weights in free radical polymerization. US 4 694 054 discloses the use of certain Co(II) complexes in emulsion polymerization.

SUMMARY OF THE INVENTION

15 This invention concerns a method for the solution or emulsion polymerization in aqueous media of at least one monomer selected from the group

- a) 1,1-disubstituted ethylenically unsaturated monomer;
- b) styrene;
- 20 c) a mixture of a and b; and
- d) a mixture of at least one of a and b with one or more other free radical polymerizable monomers;

said monomer or monomer mixture comprising at least 50 percent by weight of monomer selected from at least one of a and b;

25 comprising contacting the following materials:

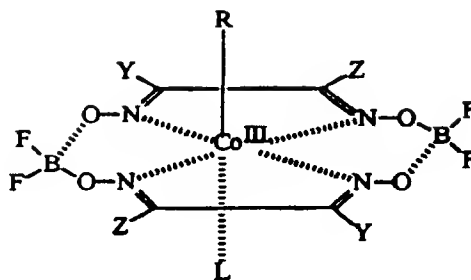
- i) water or a single phase water-organic solvent mixture,
- ii) at least one monomer selected from a to d,
- iii) a cobalt chelate chain transfer agent,
- iv) an optional surfactant for emulsion polymerization,
- 30 v) an optional free radical initiator soluble in the media;

wherein the cobalt chelate chain transfer agent has the following properties:

- vi) hydrolytic stability, and
- vii) solubility in water and in the organic phase, with preferential solubility in the organic phase.

35

We have discovered that certain types of cobalt complexes are most effective in controlling the molecular weights in emulsion polymerization or in aqueous solution. These complexes act as efficient catalytic chain transfer agents



- 5
- | | |
|-------------------------------|---|
| $\text{RCo(III)(DPG-BF}_2)_2$ | $\text{Y=Z=Ph, R= alkyl, L=ligand}$ |
| $\text{RCo(III)(DMG-BF}_2)_2$ | $\text{Y=Z=Me, R= alkyl, L=ligand}$ |
| $\text{RCo(III)(EMG-BF}_2)_2$ | $\text{Y=Me, Z=Et, R= alkyl, L=ligand}$ |
| $\text{RCo(III)(DEG-BF}_2)_2$ | $\text{Y=Z=Et, R= alkyl, L=ligand}$ |
| $\text{RCo(III)(CHG-BF}_2)_2$ | $\text{Y+Z=-(CH}_2)_4\text{- (cyclohexyl), R= alkyl, L=ligand}$ |
| $\text{RCo(III)(DMG-BF}_2)_2$ | $\text{Y=Z=Me, R= halogen, L=ligand.}$ |

10

The cobalt (III) complexes based on BF_2 -bridged 3,4-hexandione dioxime, 2,3-pentandione dioxime and 1,2-cyclohexanedione dioxime ligands are designed to give improved stability and/or solubility parameters.

- 15
- Cobalt(II) complexes [for example, $\text{Co(II)(DMG-BF}_2)_2$], although effective in emulsion polymerization, have disadvantages when used directly because of their extreme sensitivity to air. It is, therefore, preferable to use cobalt(III) complexes [for example, $\text{iPrCo(III)(DMG-BF}_2)_2$] which generate the active cobalt(II) species *in situ* under the reaction conditions. In the case of most
- 20
- alkyl cobalt (III) complexes this involves homolytic scission of the cobalt-R bond.

- Other complexes that can be used include cobalt(III) complexes which are reduced to cobalt (II) complexes in a bimolecular process involving reaction with other species in the reaction medium [for example, $\text{ClCo(III)(DMG-BF}_2)_2$ or $\text{MeCo(III)(DEG-BF}_2)_2$]. Cobalt(III) complexes which are not as readily
- 25
- converted to cobalt (II) complexes[for example $\text{MeCo(III)(DMG-BF}_2)_2$] are less effective in controlling molecular weight.

DETAILS OF THE INVENTION

- 30
- To achieve best control over molecular weight, the ligands (L) are selected to suit the reaction conditions (monomers, cosolvents, surfactant, reaction temperature, etc.). L is selected from Lewis bases including tertiary amines (such as pyridine), water, ether, phosphines, and the like, as will be obvious to one

lower reaction temperatures (50-60°C) and are preferred for polymerizations involving methacrylic acid. Organic soluble azo-compounds can also be used for emulsion polymerization in some cases.

The preferred monomers for use with this invention are α -methylvinyl and styrenic monomers, mixtures of these monomers and mixtures of these monomers with other unsaturated monomers including acrylic monomers. The preferred α -methylvinyl monomers include: alkyl methacrylates (*e.g.* MMA, EMA, *n*-BMA, *t*-BMA, 2-EHMA, PhMA, *etc.*) substituted alkyl methacrylates (*e.g.* HEMA, GMA, *etc.*), methacrylic acid (*e.g.* MAA), *etc.*.

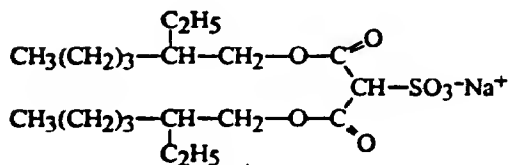
In emulsion polymerization, a wide range of surfactants and surfactant concentrations have been used in conjunction with cobalt(III) complexes. Both ionic and non-ionic surfactants may be employed. These surfactants include SDS, ADS, AerosolMA, Teric N40, Teric NX40L, alkanate, AerosolOT/Teric N40 and similar surfactants. These surfactants may be used alone or in combination.



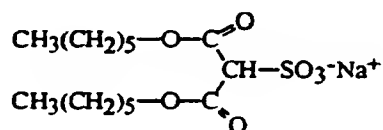
SDS



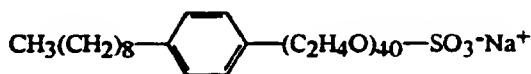
ADS



Aerosol OT



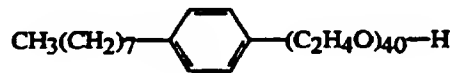
Aerosol MA80



Teric 35N5 (Alkanate)



Teric N40



Teric NX40L

Key	
MMA	methyl methacrylate
HEMA	hydroxyethyl methacrylate
nBMA	n-butyl methacrylate
tBMA	t-butyl methacrylate
PhMA	phenyl methacrylate
2-EHMA	2-ethylhexyl methacrylate
MAA	methacrylic acid
MAm	methacrylamide
GMA	glycidyl methacrylate

EXAMPLES 1-10**Emulsion polymerization with cobalt (II) complexes**

5	Initial Charge:		
	Solution 1:	Water	733 g
		Surfactant solution (30% w/v)	10.14 g
		4,4'-azobis(cyanovaleric acid)	1.32 g
10	Solution 2:	iPrCo(III)(DMG-BF ₂) ₂	0.0176 g
		MMA	35.2 g
	Solution 3:	MMA	317 g
15	Solution 4:	Water	90 g
		Surfactant solution (30% w/v)	10.98 g

20 Solution 1 was degassed over 30 minutes and heated to 80°C when solution 2 and 10% of solution 4 was added in one shot. Solution 3 and the remaining solution 4 were then added over 90 min. The reaction temperature was then held for a further 90 min. The results of this and similar experiments are summarized in Table 2.

Solution 1 was degassed over 20 minutes and heated to 80°C when solution 2 was added in one shot. The feeds (solution 3 and 4) were commenced and added over 90 min. The reaction temperature was then increased to 85°C and heating and stirring continued for a further 90 min. Results of this and similar experiments are summarized in Tables 3-5.

Table 3. Effect of Complex on Emulsion Polymerisation of MMA^a

	Example	Complex	conc ppm	\bar{M}_n	\bar{M}_w/\bar{M}_n	% Conv	% coagulum
10		none	0	181000	2.5	100	-
	11	Co(II)(DMG-BF ₂) ₂	14	29900	2.4	95	5
	12	iPrCo(III)(DMG-BF ₂) ₂	17	10000	2.2	100	4
15	13	2-octyl Co(III)(DMG-BF ₂) ₂	18	6200	1.7	34	4
	14	iPrCo(III)(CHG-BF ₂) ₂	16	18600	2.1	100	3
	15	MeCo(III)(EMG-BF ₂) ₂	16	6200	1.9	91	4
	16	MeCo(III)(DEG-BF ₂) ₂	16	3200	1.6	93	6
20							
	17	Co(II)(DPG-BF ₂) ₂	22	119200	2.5	72	1
	18	EtCo(III)(DPG-BF ₂) ₂	24	30600	1.9	92	5

^a 1% (w/v) SDS surfactant

Solution 2:	iPrCo(III)(DMG-BF₂)₂	2 mg
	MMA	3.5 g

Feed: MMA 31.7 g

Water was degassed over 20 minutes and heated to 80°C when solution 2 was added in one shot. The MMA feed was then added over 90 min. The reaction temperature was then increased to 85°C and heating and stirring continued for a further 90 min. Results are summarized in Tables 6 and 7.

Table 6. Emulsion Polymerisations of MMA - dialkylglyoxime based complexes^a

Example	Complex	conc. ppm	\bar{M}_n	\bar{M}_w/\bar{M}_n	% Conv.
34	iPrCo(III)(DMG-BF ₂) ₂	19	13400	3.68	100
35		190	1400	3.03	83
36	MeCo(III)(EMG-BF ₂) ₂	19	4300	1.87	100
37		45 ^b	2100	1.69	94
38	MeCo(III)(DEG-BF ₂) ₂	19	2900	1.58	69
39		57	920	1.65	51
40		49 ^b	730	1.70	82
41		48 ^b	900	1.78	90
42	MeCo(III)(DMG-BF ₂) ₂	46 ^b	13700	2.65	100
43			14700	2.55	100

a 1% (w/v) SDS surfactant.

b 30% of total complex added in MMA feed.

Table 7. Emulsion Polymerisation of Other Monomers^a

Example	Monomer	Complex	conc. ppm	\bar{M}_n	\bar{M}_w/\bar{M}_n	% Conv
44	n-BMA	iPrCo(III)(DMG-BF ₂) ₂	48	9800	1.8	98
45	n-BMA	MeCo(III)(DEG-BF ₂) ₂	48	5200	2.5	97
46	n-BMA	MeCo(III)(EMG-BF ₂) ₂	48	9400	2.5	100
47	t-BMA	MeCo(III)(DEG-BF ₂) ₂	43	3700	2.0	100
48	PhMA	MeCo(III)(DEG-BF ₂) ₂	43	18000	2.3	100
49	GMA	iPrCo(III)(DMG-BF ₂) ₂	109	3500	1.8	90

^a 30% of complex added with monomer feed, 1% (w/v) SDS surfactant.

min intervals to monitor molecular weight and conversion .

Yield: 105.3 g stable white latex + small amount (< 0.2 g) yellow coagulum

Table 8. Emulsion Polymerization of Styrene

Example	Monomer	Complex	conc. ppm	\bar{M}_n	\bar{M}_w/\bar{M}_n	% Conv
	Styrene	none (control)	-	130500	2.7	93
50	Styrene	MeCo(III)(DEG-BF ₂) ₂	127	44000	3.2	94
51	Styrene	MeCo(III)(DMG-BF ₂) ₂	127	48000	4.8	97

5

EXAMPLE 52

Preparation of 60:40 MAA/MMA Macromonomer

10	Initial Charge:	Deionised Water	150 g
	Solution 1	Antrox CA897	0.6 g
		Antrox CO436	0.3 g
		Initiator WAKO V-44	0.4 g
15		iPrCo(III)(DMG-BF ₂) ₂	8 mg
		MMA	4 g
	Solution 2:	iPrCo(III)(DMG-BF ₂) ₂	16 mg
		MMA	44.8 g
20	Solution 3:	MAA	28.0 g

Water (150 mL) was degassed for 20 minutes with a nitrogen purge and heated to 58°C. Solution 1 was added in one shot. The feeds (solutions 2 and 3) were then added over 60 minutes. That rate of feed two was such that 5g was added over the first 20 min, 10g over the second 20 min, and the remainder over the third 20 min. The reaction was held at 58°C for 30 minutes then heated to 65°C for 1 hour and cooled. Conversion >95%, GPC molecular weight \bar{M}_n 920, \bar{M}_w/\bar{M}_n 1.6.

30

EXAMPLES 59-62**Preparation of GMA-MMA macromonomer****Initial charge:**

	distilled water	75 g
5	SLS (3% solution)	5 g

Solution 1:

	4,4'-azobis(cyanovaleric acid)	140 mg
	GMA	2.6 g
10	MMA	1.0 g
	MeCo(III)(DEG-BF ₂) ₂	8.9 mg

Feed:

	GMA	18 g
15	MMA	13.5 g
	MeCo(III)(DEG-BF ₂) ₂	7.9 mg

20 The water-SLS mixture was vacuum degassed for 30 minutes and placed 5-neck, reactor fitted with a stirrer, condenser and a thermocouple under a blanket of nitrogen and heated to 80°C. Solution 1 was then added and the Feed commenced immediately and added over 90 minutes. The reactor was maintained at 80°C for a further 90 minutes. Conversion based on % solids was >90%.

Table 10. Emulsion Copolymerization of MMA and GMA

Example	Complex	ppm	\bar{M}_n	\bar{M}_w/\bar{M}_n
59	iPrCo(III)(DMG-BF ₂) ₂ ^a	213	790	2.04
60	iPrCo(III)(DMG-BF ₂) ₂ ^a	135	2900	1.51
61	iPrCo(III)(DMG-BF ₂) ₂	100	3620	2.13
62	MeCo(III)(DEG-BF ₂) ₂	146	1460	1.55

25 a Latex unstable

Solution 1:

4,4'-azobis(cyanovaleric acid)	140 g
iPrCo(III)(DMG-BF ₂) ₂	10 mg in 3.5 g HEMA

5 Solution 2:

HEMA	31.7 g
iPrCo(III)(DMG-BF ₂) ₂	7 mg

10 The water-methanol mixture was charged to a 5 neck, 500 mL reactor fitted with stirrer (300 rpm), condenser and thermocouple under a blanket of nitrogen and heated to 80°C. The initiator (0.14 g dissolved in 3.5 mL HEMA) and iPrCo(III)(DMG-BF₂)₂ were added to the reactor as a single shot. The feed of HEMA containing the remaining iPrCo(III)(DMG-BF₂)₂ was commenced immediately and added over 90 min. The reactor was maintained at 80°C for 150 min after the completion of the feed. Further aliquots of the initiator (70 mg) were added at 1 hourly intervals. The results of these experiments are summarized in Table 11.

Table 11. Aqueous Solution Polymerization of HEMA

Example	Complex	% solids	ppm	solvent	\bar{M}_n^a	% Conv	Colour
64	MeCo(III)(DEG-BF ₂) ₂	30	56 ^a	water	3180	93	cloudy yellow
65	iPrCo(III)(DMG-BF ₂) ₂	30	56 ^a	water	1470	87	pale yellow
66	iPrCo(III)(DMG-BF ₂) ₂	30	171 ^a	water	990	68	pale yellow
67	iPrCo(III)(DMG-BF ₂) ₂	40	343	water	530	72	pale orange
68	iPrCo(III)(DMG-BF ₂) ₂	50	400	water	490	72	pale orange
69	iPrCo(III)(DMG-BF ₂) ₂	30	162	isopropanol	420	37	dark brown
70	iPrCo(III)(DMG-BF ₂) ₂	30	160	70:30 water - isopropanol	590	30	brown
71	iPrCo(III)(DMG-BF ₂) ₂	30	105	70:30 water - methanol	1610	98	pale yellow
72	iPrCo(III)(DMG-BF ₂) ₂	30	162	70:30 water - methanol	810	68	pale yellow

20 ^a number average molecular weight estimated by NMR determination of the unsaturate end groups

minutes and the reaction mixture was allowed to reach room temperature. Half of the solvent was removed by evaporation and 40 mL of cold water was added. The compound was filtered and washed with a pyridine-water (5%) solution, and dried over P₂O₅.

5

B: Preparation of Methyl pyridinato-Co(III)-DEG BF₂ Bridged.

	Methyl pyridinato-Co(III)-DEG	3.551	g
	BF ₃ Et ₂ O	9.217	g
10	Ether	5	mL

The boron triethyletherate and ether were cooled under nitrogen at -20°C for 40 minutes. The methyl pyridinato-Co(III)-DEG was added over 20 minutes. The reaction was allowed to reach room temperature, then the compound was isolated by filtration and washed with ether.

15

C: Preparation of Methyl aqua-Co(III)-DEG BF₂ Bridged.

	Methyl pyridinato-Co(III)-DEG BF ₂ bridged	3.178	g
20	Water	30	mL

The water was degassed under nitrogen at 30°C for 10 minutes. The methyl pyridinato-Co(III)-DEG BF₂ Bridged complex was added and the solution held at 30°C for 40 minutes. The solution was allowed to reach room temperature and the compound was isolated by filtration, and washed with water

25

PROCEDURE FOR PREPARING COBALT(II) CATALYSTS

The Co(II) cobaloximes are prepared as are the Co(III) materials described above without the reaction of the intermediate with alkyl bromide, by reacting the appropriate dioxime with cobaltous chloride and bridging the reaction product with BF₃ etherate.

30

Co(II)(EMG-BF₂)₂

Y=Me, Z=Et, L=ligand

Co(II)(DEG-BF₂)₂

Y=Z=Et, L=ligand and

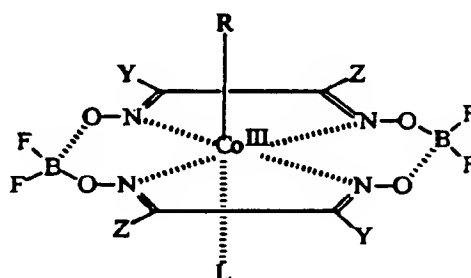
Co(II)(CHG-BF₂)₂Y+Z=-(CH₂)₄-, L=ligand.

5 4. A method according to Claim 3 wherein the cobalt chelate chain transfer agent is Co(II) (dimethyl glyoxime-BF₂)₂.

5. A method according to Claim 3 wherein the cobalt chelate chain transfer agent is Co(II) (diethyl glyoxime-BF₂)₂.

10

6. A method according to Claim 2 wherein the cobalt chelate chain transfer agent is selected from at least one member of the group



15

RCo(III)(DPG-BF₂)₂

Y=Z=Ph, R= alkyl, L=ligand

RCo(III)(DMG-BF₂)₂

Y=Z=Me, R= alkyl, L=ligand

RCo(III)(EMG-BF₂)₂

Y=Me, Z=Et, R= alkyl, L=ligand

RCo(III)(DEG-BF₂)₂

Y=Z=Et, R= alkyl, L=ligand

20

RCo(III)(CHG-BF₂)₂Y+Z=-(CH₂)₄-, R= alkyl, L=ligand andRCo(III)(DMG-BF₂)₂

Y=Z=Me, R= halogen, L=ligand.

7. A method according to Claim 6 wherein the cobalt chelate chain transfer agent is alkylCo(III) (dimethyl glyoxime-BF₂)₂.

25

8. A method according to Claim 6 wherein the cobalt chelate chain transfer agent is alkylCo(III) (diethyl glyoxime-BF₂)₂.

9. A method according to Claim 1 wherein the polymer formed is a macromonomer.

30

10. A cobalt chelate chain transfer agent selected from the group:

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 95/14429A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/38 C08F2/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP,A,0 199 436 (DU PONT DE NEMOURS AND COMPANY) 29 October 1986 cited in the application see claims 1-10 ---	1-10
X	US,A,4 526 945 (G. M. CARLSON) 2 July 1985 see the whole document ---	1,2,9
X	US,A,4 680 354 (JU-CHUI LIN) 14 July 1987 see the whole document ---	1,2,9
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 March 1996

Date of mailing of the international search report

- 4. 04. 96

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Permentier, W

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/14429

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